Renormalization of Molecular Quasiparticle Levels at Metal-Molecule Interfaces: Trends Across Binding Regimes

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When an electron or a hole is added into an orbital of an adsorbed molecule the substrate electrons will rearrange in order to screen the added charge. This results in a reduction of the electron addition/removal energies as compared to the free molecule case. In this work we use a simple model to illustrate the universal trends of this renormalization mechanism as a function of the microscopic key parameters. Insight of both fundamental and practical importance is obtained by comparing GW quasiparticle energies with Hartree-Fock and Kohn-Sham calculations. We identify two different polarization mechanisms: (i) polarization of the metal (image charge formation) and (ii) polarization of the molecule via charge transfer across the interface. The importance of (i) and (ii) is found to increase with the metal density of states at the Fermi level and metal-molecule coupling strength, respectively.

The position of an adsorbed molecule's frontier orbitals with respect to the substrate Fermi level determines the threshold energies at which electron transfer can take place across the metal-molecule interface. Such electron transfer processes represent a cornerstone of surface science and form the basis of photo- and non-adiabatic chemistry, organic- and molecular electronics, as well as scanning tunneling- and photoemission spectroscopy [1, 2, 3, 4, 5, 6, 7]. Accurate descriptions of adsorbate energy spectra are thus fundamental for quantitative modeling within these important areas.

Recently, a number of experiments probing transport- and optical properties of molecules at metal surfaces, have found strong reductions of electron addition/removal energies due to polarization effects in the metal substrate [4, 5, 6, 7, 8], see Fig. 1a. Theoretical studies of metal-molecule interfaces are usually based on density functional theory (DFT) and rely on an interpretation of Kohn-Sham (KS) eigenvalues as quasiparticle energies. This interpretation is unjustified in principle and questionable in practice – even with the exact exchange-correlation functional – because single-particle schemes like KS and Hartree-Fock (HF) take no account of dynamical effects such as screening of added electrons/holes. Inclusion of dynamical polarization effects through classical image charge models have been applied to correct DFT calculations of quantum transport in molecular contacts [9, 10, 11]. Only recently, GW calculations by Neaton *et al.* have demonstrated that the energy gap of benzene is reduced by more than 3 eV when physisorbed on graphite due to image charge effects.[12] As a complementary study, the present work focuses on qualitative trends and explores different binding situations including strong-weak coupling and narrow-wide band substrates.

To illustrate the problem, suppose we add an electron into the lowest unoccupied orbital (LUMO) of an adsorbed molecule. The associated energy cost is given by the quasiparticle (QP) spectral function

$$A_L(\varepsilon) = \sum_n |\langle \Psi_n^{N+1} | c_L^\dagger | \Psi_0^N \rangle|^2 \delta(\varepsilon - E_n^{N+1} + E_0^N), \quad (1)$$

where $|\Psi_0^N\rangle$ and $|\Psi_n^{N+1}\rangle$ denote the many-body N-particle groundstate and $(N + 1)$-particle excited states, respectively. The qualitative shape of A_L is mainly dictated by the hybridization with the metal states. On the other hand, quantitative features such as the precise position of its peak(s), depend on the system's response to the extra electron in the LUMO. This follows by noting that peaks in A_L appear at dominant Fourier components of $c_L^\dagger |\Psi_0^N\rangle(t)$. Dynamical effects of this type can be incorporated within an effective single-particle framework where the electron-electron interaction is represented by an energy-dependent potential known as a self-energy. In practice the self-energy must be approximated using e.g. many-body perturbation theory. For weak metal-molecule coupling, total energy calculations with constrained occupations of the molecule represent a simple alternative to the many-body approach. [13] However, such calculations only provide a lower (upper) limit for the LUMO (HOMO) energy and, as we show here, these limits can differ from the true quasiparticle levels.

In this Letter, we introduce a simple model of a metal-molecule interface and use it to investigate the effect of dynamical polarization on the molecular levels as a function of microscopic key quantities such as the metal-molecule coupling strength (Γ) and the metal density of states (DOS). We find that polarization effects consistently reduce the molecular gap as compared to the gas phase value. This effect is completely absent in HF
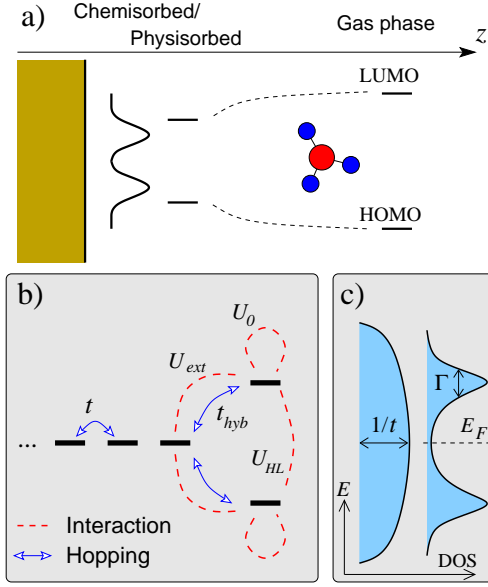
FIG. 1: (Color online) (a) Schematic of a molecule's HOMO and LUMO energy levels as it approaches a metal surface. For weak coupling (physisorbed molecule) the gap is reduced due to image charge formation in the metal. For strong coupling (chemisorbed molecule) dynamic charge transfer between molecule and metal reduces the gap further. (b) The model used in the present study. (c) The semi-elliptical band at the terminal site of the TB chain and the resonances of the molecule.

theory which systematically overestimates the gap. On the other hand, the KS spectrum is indirectly affected through the "exact density" requirement, however, the KS gap is always found to be too small. On the basis of GW calculations, we find that the gap reduction due to polarization of the metal, i.e. image charge formation, is insensitive to Γ but increases with the metal DOS at E_F. On the other hand, polarization of the molecule via charge transfer to/from the metal increases strongly with Γ leading to a direct correlation between adsorbate bond strength and the gap renormalization.

Our model Hamiltonian consists of three parts, $\hat{H} = \hat{H}_{\text{met}} + \hat{H}_{\text{mol}} + \hat{V}$, describing the metal, the molecule, and their mutual interaction, see Fig. 1b. The metal is modeled by a non-interacting, semi-infinite tight-binding (TB) chain,

$$\hat{H}_{\text{met}} = \sum_{i=-\infty}^{0} \sum_{\sigma=\uparrow,\downarrow} t(c_{i\sigma}^{\dagger}c_{i-1\sigma} + c_{i-1\sigma}^{\dagger}c_{i\sigma}). \quad (2)$$

The molecule is modeled as two interacting levels representing the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals

$$\hat{H}_{\text{mol}} = \xi_H \hat{n}_H + (\xi_H + \Delta_0)\hat{n}_L + \hat{U}_{\text{mol}} \quad (3)$$

$$\hat{U}_{\text{mol}} = U_0 \hat{n}_{H\uparrow}\hat{n}_{H\downarrow} + U_0 \hat{n}_{L\uparrow}\hat{n}_{L\downarrow} + U_{HL}\hat{n}_H \hat{n}_L, \quad (4)$$

where e.g. $\hat{n}_H = c_{H\uparrow}^{\dagger}c_{H\uparrow} + c_{H\downarrow}^{\dagger}c_{H\downarrow}$, is the number operator of the HOMO level. Notice that, despite the interactions, the eigenstates of $\hat{H}_{\text{mol}}$ are simply Slater determinants build from the orbitals $|H\sigma\rangle$ and $|L\sigma\rangle$. Finally, hybridization and interaction between the molecule and the terminal site of the chain is described by

$$\hat{V} = \sum_{\nu=H,L} \sum_{\sigma=\uparrow,\downarrow} t_{\text{hyb}}(c_{0\sigma}^{\dagger}c_{\nu\sigma} + c_{\nu\sigma}^{\dagger}c_{0\sigma}) + U_{\text{ext}}\delta\hat{n}_0\delta\hat{N}_{\text{mol}}.$$
$$(5)$$

Here $\delta\hat{n}_0 = (\hat{n}_0 - 1)$ and $\delta\hat{N}_{\text{mol}} = (\hat{N}_{\text{mol}} - 2)$ represent the excess charge on the chain's terminal site and the molecule, respectively. We set $E_F = 0$ corresponding to a half filled band, and adjust ξ_H so that the molecule holds exactly two electrons in the groundstate. Specifically this means $\xi_H = -\Delta_0/2 - U_0/2 - U_{HL}$. The model neglects interactions within the TB chain and between the molecule and interior TB sites ($i < 0$). These approximations are, however, not expected to influence the qualitative trends described by the model.

It is instructive first to consider the model in the limit $t_{\text{hyb}} = 0$ (weak physisorption) where the metal and molecule interact only via the Coulomb term $\hat{U}_{\text{ext}}$. It is straightforward to verify that in this limit, the many-body eigenstates coincide with the HF solutions. More precisely they are single Slater determinants constructed from the molecular orbitals, $|H\sigma\rangle$ and $|L\sigma\rangle$, and the eigenstates of the Hamiltonian, $\hat{H}_{\text{met}}^{\text{HF}}(\delta N_{\text{mol}}) = \hat{H}_{\text{met}} + U_{\text{ext}}\langle\delta\hat{N}_{\text{mol}}\rangle\hat{n}_0$, where $\langle\delta\hat{N}_{\text{mol}}\rangle = -2, \ldots, 2$ is the number of molecular orbitals in the Slater determinant. Although the eigenstates are single Slater determinants, the situation is different from the non-interacting case because the single-particle orbitals of the metal depend on the occupation of the molecule (each electron on the molecule will shift the potential of the terminal site by U_{ext}). As we will see below this has important consequences for the position of the molecule's QP levels.

In order to test the accuracy of the GW approximation for the problem at hand, we have compared it to exact diagonalization results in the case where the TB chain is truncated after the first two sites, see the supplementary material. [14] The GW spectral function is essentially identical to the exact result, also for strong interactions, demonstrating that GW captures the essential physics of the model accurately.

To study how the molecular levels depend on the model parameters, we vary one parameter at a time keeping the remaining fixed at the following reference values: $t = 10$, $t_{\text{hyb}} = 0.4$, $U_0 = 4$, $U_{HL} = 3$, $U_{\text{ext}} = 2.8$, $\Delta_0 = 2$. The reference values correspond to weak coupling ($\Gamma \approx 0.02$) and a wide-band metal ($W = 4t = 40$). The positions of the HOMO and LUMO levels are defined as the maximum of the corresponding spectral functions (1) which we calculate from the Green's function, $A_n(\varepsilon) = -(1/\pi)\text{Im}G_{nn}^r(\varepsilon)$, see supplementary material for plots of a representative set of spectral functions [14].
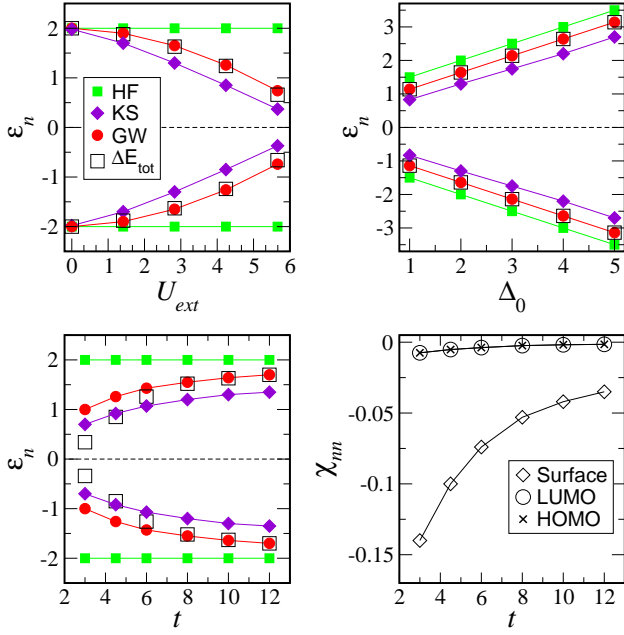
FIG. 2: (Color online) Position of the HOMO and LUMO levels as a function of different model parameters for a weakly coupled molecule (small Γ). Note that dynamical polarization is completely absent in HF theory and incorrectly described by the "exact" KS theory. Open squares denote the exact total energy difference between the normal groundstate and the groundstate when the molecule has been constrained to hold one extra electron/hole. Lower right panel shows on-site elements of the static, linear response function of the HOMO, LUMO and terminal site of the TB chain. Clearly, the renormalization of the gap is due to polarization of the metal.

The Green's function is obtained by solving the Dyson equation fully self-consistently in conjunction with the self-energy ($\Sigma_{GW}[G]$ or $\Sigma_{HF}[G]$) as described in Ref. [15]. Following the lattice version of DFT [16], we define the KS Hamiltonian as the non-interacting part of $\hat{H}$ with the on-site energies corrected to yield the exact occupation numbers. Using the GW occupations as "exact" target occupations this allows us to obtain the "exact" KS levels.

In the upper left panel of Fig. 2 we show the position of the molecule's QP levels as function of the metal-molecule interaction, U_{ext}. The GW gap decreases as U_{ext}^2. The reduction of the gap corresponds to the energy gained by letting the HF states of the metal relax in response to the added electron/hole, i.e. to the perturbations $\pm U_{ext}\hat{n}_0$. Indeed, the open squares show the difference in total energy between the normal groundstate and the groundstate when the molecule has been constrained to hold one extra electron/hole.[17] HF completely misses this effect due to its neglect of orbital relaxations, and consequently the HF gap becomes too large. In a screening picture, the difference between the HF and

GW levels equals the binding energy between the added electron/hole and its image charge (the positive/negative induced density at the terminal site), corrected by the cost of forming the image charge.

The "exact" KS theory underestimates the gap, but seems to reproduce the trend of the GW calculation. At first this is surprising since a mean-field theory cannot describe the dynamical effects responsible for the gap reduction. The explanation is that the KS levels are affected *indirectly*: the KS levels are forced to follow the GW levels in order to reproduce the GW occupations.

In the upper right panel of Fig. 2 we show the dependence of the QP levels on the molecule's intrinsic gap, Δ_0. The fact that the renormalization of the QP gap due to image charge formation is independent of Δ_0 follows from the discussion above since $\hat{H}_{met}^{HF}$ is independent of Δ_0.

It seems intuitively clear that the size of the gap reduction (for fixed U_{ext}) should depend on the polarizability of the metal, i.e. how much the electron density changes in response to the perturbing field created by the added electron/hole. In the lower left panel of Fig. 2 we show the QP levels as function of the chain hopping, t.[18] The gap reduction is larger for small t corresponding to a narrow band. This is easily understood by noting that a narrow band implies a large DOS at E_F which in turn implies a larger density response function. In the lower right panel of Fig. 2 we show the diagonal elements of the static component of the response function, $\chi_{nn}(\omega = 0)$, for the HOMO, LUMO and terminal site of the chain, respectively. In this weakly coupled regime, the response function of the HOMO and LUMO is clearly negligible for all values of t, while the response of the terminal site is significant and increases as t is reduced. This clearly demonstrates that the QP levels are renormalized by screening inside the metal. In general, only the response at frequencies $|\omega| \leq \Gamma$ is relevant as Γ^{-1} sets the decay time of the states $c_L^\dagger|\Psi_0\rangle$ and $c_H|\Psi_0\rangle$.

Interestingly, the deviation between the GW levels and ΔE_{tot} becomes significant for small t. We stress that this does not imply that the GW results are wrong. In fact, ΔE_{tot} only represents an upper/lower bound for the true QP energies, and the deviation thus indicates that the overlap of $c_L^\dagger|\Psi_0\rangle$ and $c_H|\Psi_0\rangle$ with higher lying excited states of the $(N+1)$-particle system (see Eq. (1)) is more important for small t.

We now leave the regime of weak molecule-metal coupling and consider the dependence of the molecular spectrum on t_{hyb}, see Fig. 3. At finite t_{hyb} the molecular levels broaden into resonances, however, it is still possible to define the level position as the resonance maximum.[19] In addition to the GW, HF, and KS levels, we also show the result of a calculation where only $\hat{U}_{mol}$ is treated at the GW level while $\hat{U}_{ext}$ is treated at the HF level. This means that the only dynamical effects included in the GW(mol) calculation are those due to $\hat{U}_{mol}$. In particu-
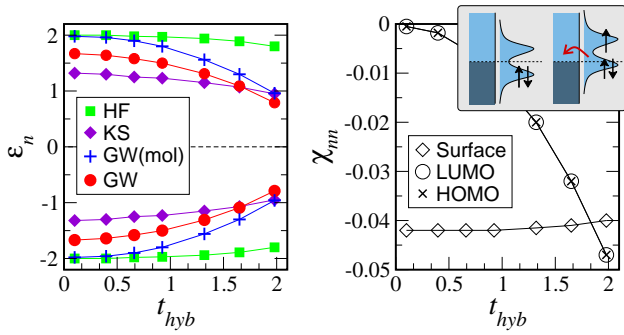
FIG. 3: (Color online) Left: Position of the molecule's HOMO and LUMO levels as a function of the hybridization strength, t_{hyb}. GW(mol) refers to a calculation where only the internal interactions on the molecule, $\hat{U}_{\mathrm{mol}}$, have been treated within GW while the interactions with the metal, $\hat{U}_{\mathrm{ext}}$ have been treated within HF. Right: Static response function for the HOMO, LUMO, and terminal site of the TB chain. The cartoon illustrates how dynamic charge transfer stabilizes the charged system and thereby reduces the gap.

lar, image charge formation in the metal is ignored.

Focusing on the GW and GW(mol) results, we conclude that the reduction of the QP gap as function of t_{hyb} is mainly due to the interactions internally on the molecule. On the other hand, the reduction due to the molecule-metal interaction is largely insensitive to t_{hyb} (this reduction is given by the difference between the GW and GW(mol) levels). From the right panel of Fig. 3, we see that $|\chi_{nn}|$ for the HOMO and LUMO states increases with t_{hyb} indicating that the gap reduction due to $\hat{U}_{\mathrm{mol}}$ is of a similar nature as the image charge effect, but with the molecule itself being polarized instead of the metal. Polarization of the molecule can occur via dynamic charge transfer to/from the metal as illustrated in the cartoon of Fig. 3. Note that this picture is consistent with the fact that no polarization of the molecule occurs without coupling to the metal (see GW(mol) result in the limit $t_{\mathrm{hyb}} \to 0$ in Fig. 3).

The fact that dynamical polarization becomes more important as the molecular DOS at the Fermi level increases, has important consequences for charge transport in molecular junctions. Indeed, as the chemical potential, μ_α, approaches a molecular level, polarization effects become stronger and the level is shifted towards μ_α. This effect was recently shown to have a large impact on the junction IV characteristics. [20] Finally, we mention that the correlation between chemisorption bond strength and gap renormalization suggested by Fig. 3, has in fact been observed in inverse photoemission spectroscopy experiments.[7]

In summary, we have used a simple model of a metal-molecule interface to identify universal trends in the way dynamical polarization renormalize molecular interface states. The effect of polarization is to reduce the gap be-

tween occupied and unoccupied molecular orbitals. The size of the gap reduction correlates directly with the static response function, and is promoted by larger metal and/or molecular DOS at the Fermi level. The latter suggests that transition metals with half-filled d band should be more effective in reducing the gap of molecular adsorbates than e.g. alkali, sp, and the early/late transition metals. The results strongly indicate that dynamical polarization is of fundamental importance for charge transfer at metal-molecule interfaces.

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[18] We stress that even though Γ depends on t, all results of Fig. 2 are essentially unchanged as t_{hyb} is reduced below the reference value and thus represent the limit $t_{\mathrm{hyb}} \to 0$.
[19] Due to the interactions, the resonance width is slightly enlarged relative to the non-interacting value of $\Gamma^{-1} \approx |t|/|t_{\mathrm{hyb}}|^2$.
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